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NATIONAL GAS TURBINE ESTABLISHMENT

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N.G.T.E. REPORT. No. R. 267

INVESTIGATION INTO THE RESISTANCE OF VARIOUS NICKEL AND COBALT BASE ALLOYS TO SEA-SALT CORROSION AT ELEVATED TEMPERATURES

by

A. V. DEAN

MAY 1965

NATIONAL GAS TURBINE ESTABLISHMENT

Investigation into the resistance of
various nickel and cobalt base alloys
to sea-salt corrosion at elevated temperatures

- by -

A. V. Dean

SUMMARY

Gas turbines operating in salt laden atmospheres (i.e., over the sea) occasionally encounter severe corrosion of the turbine blades. The cause of this attack is attributed to ingested sea-salt combining in the combustion chamber with the sulphur in the fuel to form sodium sulphate which is deposited on the turbine blades and leads to corrosive attack. Laboratory investigations at N.G.T.E. have involved the passage over heated specimens of the vapours and gases (e.g., sodium chloride and sulphur dioxide) that were thought most likely to cause corrosion. Tests at 950°C indicated that nickel-base alloys low in chromium were very susceptible to attack, but that a high chromium content alone was insufficient to ensure good corrosion resistance. However, the presence of adequate amounts of aluminium in the alloys appeared to be beneficial. The corrosion resistance of cobalt-base alloys was no better than that of nickel-base alloys.

A corrosion mechanism is proposed which involves the depletion of chromium from the surface of the alloy through sulphide formation so leading to a loosely-adherent nickel oxide film. Adequate percentages of aluminium in nickel-base alloys are thought to have a beneficial effect because aluminium does not form a stable sulphide and is therefore always available in the surface layers of the alloy to form protective aluminium oxide.

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1.0   Introduction

Alloys based on iron, nickel or cobalt are well known for their good resistance to oxidation at temperatures of 1200°C or more. However, in service, corrosive media other than air are frequently encountered and can lead to catastrophic component failure.

The three types of fuel commonly used in turbines are coal, fuel oil and diesel oil and their combustion products are found to contain particularly reactive elements such as sulphur, vanadium, chlorine and sodium[1]. Vanadium, as the pentoxide, collects in the ashes resulting from the combustion of fuels such as residual oil and coal and corrodes those parts with which it comes into contact. Sulphur readily enters into combination with oxygen and sodium to form sulphur dioxide, sulphur trioxide and sodium sulphate. Corrosion in boilers has been encountered for many years and results from the use of fuels containing relatively large percentages of vanadium, sulphur etc. Coal, for example, can contain as much as 5 per cent sulphur.

In comparison, fuel oils for gas turbines have sulphur contents of 1 per cent or less and can be as low as 0.1 per cent for aircraft gas turbine applications[2,3]. (The specified maximum for aviation kerosine is 0.2 per cent but invariably the content is less than 0.1 per cent.) In recent years, however, severe corrosion of gas turbine rotor and stator blades has occasionally been reported and is giving cause for concern. This corrosion has occurred on the blades of turbines operating in salt laden atmospheres (i.e., operating over the sea) and appears to be associated with salt ingested into the engine.

The N.G.T.E. Materials Department became interested in this problem following a report by the United States Navy that turbine blade corrosion could be eliminated by the use of cobalt alloys instead of nickel alloys[4]. Following discussions between the Admiralty and the Bureau of Ships in Washington, it transpired that this claim was not based on any experimental evidence. It was therefore decided to examine the problem and determine the laboratory corrosion resistance of blade alloys and of compositions potentially resistant to sea-salt corrosion.

2.0   Review of corrosion experience in British engines

Some of the earliest engine tests under simulated sea-air conditions were carried out by Bristol Siddeley Engines Limited in 1955 using their Marine Proteus engine[2,5,6]. This turbine has wide usage in powering fast Naval craft and was particularly susceptible to sea-salt ingestion due to the air intake being positioned near to the level of the sea. Engine testing lasted 225 hr using a diesel fuel containing 0.57 per cent sulphur and sea water injection to give a salt concentration of 1.07 p.p.m. in the intake air. Examination, after completion of the test, revealed that the Nimonic 90 nozzle guide vanes had experienced considerable corrosion. Laboratory investigations of the deposits on the stator segments showed that 8.3 per cent was water soluble and was chiefly composed of sodium sulphate plus a little calcium and magnesium sulphate. No chloride was present. The non-solubles consisted of the oxides of nickel, cobalt, titanium, iron, chromium, aluminium and silicon. A small amount of carbonaceous material (thought to be carbonised fuel) was also present. X-ray diffraction studies showed the outer corrosion layer to be largely nickel oxide (NiO) with cobalt sulphide (Co_3S_4) present. The intermediate

layer contained nickel and nickel sulphide (Ni_3S_4) and was substantially metallic and magnetic. The magnetic state indicated a loss of chromium from this layer.

The important feature of the test was the presence of 8 per cent sodium sulphate in the deposits found on the nozzle guide vanes. It is probable that this sulphate was formed in the combustion chamber as a result of interaction of sodium chloride from the sea-salt with sulphur dioxide (or trioxide) derived from the sulphur in the fuel. The absence of attack on the first stage and subsequent rotor blades is significant. In the Proteus engine test the stator blades, operating at 900° to $930^\circ C$, were considerably more susceptible to corrosive attack than the subsequent rotor and stator blades that were operating at least $80^\circ C$ lower, thus indicating the influence that temperature may play in promoting attack.

Other early experiments were carried out by Metropolitan Vickers[2] with their Gatric engine in MGB.2009, the first gas turbine-powered sea craft. The purpose of these trials was to determine the problems resulting through salt ingestion into such engines. Despite air inlet design modification, considerable amounts of sea-salt entered the engine and some slight corrosion of the nozzle guide vanes (manufactured from Nimonic 80) was encountered. Analysis of the corrosion products showed that they consisted of approximately 95 per cent nickel sulphate ($NiSO_4$ $7H_2O$), 4 per cent sodium chloride, and about 1 per cent carbonaceous matter.

Trials were also carried out with a Metropolitan Vickers G2 engine[2] in H.M.S. 'Bold Pathfinder'. Particularly severe conditions were encountered in this test, and melting of the nozzle guide vanes (Nimonic 80A) was encountered due to overheating to temperatures of about $1450^\circ C$ for short periods. Blades that had not been heated above 850 to $870^\circ C$ were unattacked. Blades that had reached temperatures in excess of 850 to $870^\circ C$ showed very marked corrosion, characterised by a green deposit. Analysis of the deposits revealed a predominance of sodium sulphate with traces of nickel and chromium.

More recently (1961), Napier Aero Engines Limited[7], carried out helicopter trials using their Gazelle 101 engine. After 150 hr hovering, of which 30 hr was actually over the sea, the Nimonic 100 blades showed nibbled edges and slight greenish scale. Further tests[8,9] with controlled sea water ingestion were also carried out. The initial running used ingestion equivalent to 25.4 p.p.m. of salt, but, due to drop in engine power, the ingestion was subsequently reduced to less than 1 p.p.m. The fuel used had a sulphur content of approximately 1 per cent. After 30 hr, severe corrosion of the Nimonic 100 first stage rotor blades, particularly along the trailing edges, had occurred (see Figure 1). Microscopic study revealed that the corroded areas consisted of an outer loosely-adhering oxide scale over a metal plus oxide layer. Beneath this intermediate layer a finely dispersed layer (probably sulphide) embedded in the matrix could be seen (see Figure 2). The few naval helicopters in current service are powered by Nimbus engines which apparently have not encountered corrosion. The use of low sulphur (~ 0.1 per cent) Avcat fuel, short flying durations and frequent engine inspection and component replacement may minimise any corrosion effects.

Similar corrosion was reported by Bristol Siddeley Engines Limited,[10] after more recent trials with their Proteus engine installed in H.M.S. 'Brave Borderer'. After over 700 hr running, pitting on the

surface of the Nimonic 90 rotor blades was detected and led to a full laboratory examination. Figure 3 shows a typical blade removed from the engine. A section through a corroded area, about 0.03 in. diameter and 0.004 in. deep, is shown in Figure 4. The outermost layer consisted entirely of oxide whereas the innermost was found to be chromium sulphide which had a typical grey appearance. The intermediate layer was darker in colour and was thought to be a mixture of sulphide and oxide.

The ease with which corrosion attack can unexpectedly occur in service is well illustrated in Figures 5 and 6. In this case omission to replace a hatch resulted in substantial amounts of sea water being ingested into a Proteus engine installed in H.M.S. 'Bravo Borderer'[4]. A segment of a first stage stator showing severe corrosion of the Nimonic 90 blades is illustrated in Figure 5.

The most recently encountered catastrophic failure occurred in an Allen turbine alternator installed in an Ashanti class frigate[11,12]. Microscopic examination again showed typical sea-salt corrosion. The deposits were found to contain sulphur and sodium. Analysis of the scale is shown in Table I and may be compared with the normal alloy composition. The probability of excessive temperatures being incurred during the operation of this engine is of particular significance, again indicating the effect that high temperatures may have in assisting corrosive attack.

All the corrosion examples cited above occurred in gas turbine engines installed in sea craft which understandably ingest air heavily laden with salt. No turbine blade corrosion has been experienced in aircraft engines of the Fleet Air Arm[2]. Because deck running time is quite limited and sea-salt concentration falls off rapidly with height above sea level engine running will be mostly in unpolluted air.

From the engine experience certain conclusions can be drawn concerning the nature of this corrosion. These are summarised below:-

(a)   Fuels used in gas turbines installed in sea-faring craft can contain as much as 0.6 per cent sulphur but under normal conditions (i.e., no salt ingestion) this does not result in corrosion of the turbine blades.

(b)   Ingestion of even very small amounts of sea-salt (i.e., 1 p.p.m.) can result in severe corrosion of turbine blading. This has become known as 'sea-salt corrosion'. Typical sea-salt may contain as much as 80 per cent sodium chloride with small quantities of other salts (see Table II).

(c)   Analysis of deposits found on corroded blades reveals substantial amounts of sodium sulphate but usually no sodium chloride. It appears that the sodium chloride present in the ingested sea-salt combines with the sulphur in the fuel to form sodium sulphate which is finally deposited on the stator and rotor blades.

(d)   Corrosion appears as a heavy outer oxide scale over an intermediate layer of oxide plus sulphide. The innermost layer is comprised of chromium sulphide which is formed preferentially to nickel sulphide. The presence of sulphide in the corrosion products indicates the significant part sodium sulphate may play in promoting attack.

(e)   Sea-salt corrosion of blades that do not reach particularly
        high temperatures ($\downarrow$850°C) (i.e., second and subsequent
        stages of rotors and stators) has not been reported, whereas
        engines which have overheated often showed very severe cor-
        rosion of the nozzle guide vanes and first stage rotors.
        Therefore temperature may have a marked influence in the
        initiation and degree of corrosion.

(f)   Turbine blades manufactured from a range of nickel-base
        alloys (i.e., Nimonics 80, 80A, 90 and 100) have been
        corroded in engine trials in salt laden atmospheres. This
        suggests that no current rotor blade alloy possesses out-
        standingly good resistance to this type of corrosion.

3.0   Laboratory investigations of sea-salt corrosion

Although sodium sulphate is quite innocuous, the presence of
certain impurities, especially sodium chloride, could lead to corrosion
of gas turbine blades. Accepting this hypothesis, many investiga-
tors[13,14,15] have studied the corrosive effects of sodium sulphate/
sodium chloride mixtures on various turbine blade materials. Testing
has involved the half-immersion of cylindrical specimens in salt mix-
tures at temperatures up to 1000°C for durations of 1 to 88 hr. Salt
mixtures ranging in composition from pure sodium sulphate to 50 per cent[15]
by weight sodium chloride have been used, although it has been suggested
that salt mixtures containing 0.5 to 1.0 per cent chloride have a corro-
sive effect similar to the deposits found on blades in service.

The most comprehensive corrosion study with salt mixtures was
carried out by Lewis and Smith[15] in which they determined the effect of
salt mixtures containing 0 to 50 per cent sodium chloride on various
nickel-base alloys at temperatures from 700 to 1000°C. Results obtained
with salt mixtures low in chloride bore no relation to results obtained
with mixtures containing high percentages of chloride. True alloy com-
parison was therefore impossible. This is well illustrated by comparing
the data shown in Figures 6 and 7. Comparison between the various inves-
tigators also yields widely differing conclusions. It is clear from the
available data that the Nimonic type alloys (no data available for
Nimonic 115) are vulnerable to attack in salt mixtures.

Due to the high volatility of sodium chloride and its readiness
to combine with sulphur from the fuel, its absence from analysed deposits
on blades is not unexpected. It has been recently suggested that sea-
salt particles present in the secondary air supplied to the combustion
chamber may still exist as particles upon reaching the first blade stages[4].
However, this still remains to be verified. Salt particles successful
in reaching the turbine would also have to penetrate the sulphate deposit
in order to trigger reaction between blade alloy and sulphate deposit.
Therefore, although sodium chloride readily initiates the corrosion of
nickel alloy specimens half-immersed in salt mixtures it is far from
conclusive that a similar phenomenon occurs in service.

Simple laboratory tests show that carbon, like sodium chloride,
is able to initiate corrosion of nickel alloys by sodium sulphate. It is
possible, therefore, for carbon to have a similar effect in the gas tur-
bine where incandescent particles of carbon passing through the engine are

deposited on the first row stators and rotors[16], and are therefore readily available to reduce the sodium sulphate.

4.0   Laboratory investigations at N.G.T.E.

A research programme was initiated to determine the relative resistance of various nickel and cobalt base alloys to sea-salt corrosion and also to shed further light on the mechanism of attack. The 'half-immersion' type of test, using mixtures of sodium sulphate and sodium chloride, was not considered to be sufficiently realistic and attempts have been made at N.G.T.E. to produce corrosion conditions in the laboratory more similar to those occurring in service. Tests have involved the passage over heated test specimens of gases and vapours thought most likely to cause corrosion. A suitable rig was designed and built and is shown diagrammatically in Figure 8.

The apparatus consists essentially of a long alumina tube passing through two independently controlled furnaces with a means for introducing gaseous sulphur dioxide, sodium chloride vapour, and water vapour into the airstream. Sodium chloride was introduced into the gas stream by passing air through and over lumps of sodium chloride dispersed in alumina, heated to a known temperature in the first furnace (Tube A). Reasonable temperature control ($\pm 7^\circ$C) was attained over much of the length (14 in.) of each furnace by using three separately-wound furnace elements. The second furnace (Tube B) was used for heating two cylindrical specimens (generally 1 cm diameter x 2 cm long) to the test temperature ($\pm 1^\circ$C).

A gas flow rate of 4 litres/min saturated with water vapour was used for all tests. By selecting a suitable temperature, the vapour pressure of sodium chloride, and therefore the amount of vapour taken up by the air, could be adjusted to the requisite amount. A graph relating vapour pressure and temperature for sodium chloride[17] is shown in Figure 9. Temperatures of 618 and 692°C gave salt contents of 5 and 50 p.p.m. in the gas stream. In service the amount of salt ingested into an engine is quite variable, depending on proximity to sea, and severity of wind and sea turbulence. Under widely differing conditions the amount of salt ingested can vary between 1 and upwards of 25 p.p.m. For this reason laboratory tests have been carried out using salt contents of 5 and 50 p.p.m. in the gas stream. Analytical checks on the salt content verified these concentrations.

Gaseous sulphur dioxide is introduced into the gas stream between Tubes A and B as shown in Figure 8. The lowest flow rate used gave a sulphur dioxide content of about 0.045 per cent which is equivalent to about ten times that likely to be found in the combustion chamber of an aircraft gas turbine. The gas stream containing sodium chloride vapour, sulphur dioxide, and water vapour now passes along Tube B and over the heated alloy specimens. Using this apparatus corrosion tests have been carried out at temperatures up to 1000°C for duration of 100 hr or more and the results obtained are reported below.

Comparative laboratory half-immersion tests (using a 75 per cent sodium sulphate, 25 per cent sodium chloride mixture) were also carried out on various nickel and cobalt base alloys in the form of cylindrical specimens immersed for 1 hr at 950°C.

5.0   Laboratory test results

A preliminary series of tests were carried out at 950°C using a sodium chloride concentration of 5 p.p.m. and a sulphur dioxide concentration of 0.045 per cent. These concentrations are approximately ten times those likely to be encountered in a gas turbine operating in normal conditions just above the sea. These initial tests on some typical turbine blade alloys resulted in negligible corrosion. Carbon was therefore introduced into the experiment to determine whether its presence had a triggering effect on the corrosion reaction. Cylindrical specimens were given dip coatings of graphitic carbon suspended in ethyl alcohol ('Dag') and then exposed to the gas stream. Prolonged exposure at 950°C resulted in substantial attack on the same alloys.

Metallographic examination revealed that alloy specimens corroded in these laboratory tests had experienced corrosion very similar in appearance to that encountered in service on similar alloys. This is well illustrated by comparing Figures 10 and 11 with Figure 2. Beneath the outer loosely-adherent oxide scale a layer consisting of a mixture of black oxide and grey sulphide can be clearly seen. "Fingers" of grey sulphide penetrating into the underlying alloy matrix form the innermost layer. The presence of sulphate in the outermost scale was chemically identified.

The results obtained for a number of nickel and cobalt base alloys at 950°C for durations up to 100 hr or more are summarised in Table III. Typical compositions of the various alloys tested are given in Appendix I. Nimonics 75, 80A and 90 were found to have good resistance to attack under the test conditions. Nimonic 100 with a chromium content of 10 to 12 per cent (compared with about 20 per cent for Nimonics 75, 80A and 90) has particularly poor resistance. The casting alloy, Nimocast 258, of similar composition to Nimonic 100, was also found to have poor resistance to corrosion. Evidently the high aluminium content (5 to 6 per cent) of Nimonic 100 and Nimocast 258 does not compensate for low chromium content. In comparison, Nimonics 105 and 115, having intermediate chromium contents (~15 per cent) but similar aluminium contents (~5 per cent), showed very good corrosion resistance.

Several other nickel-base alloys (i.e., C26, Alloy C, E474, EPD13 and chromium-nickel (60/40)), were included in the tests although they are unlikely to be considered for turbine blade applications because of their brittleness or inadequate strength. Of these alloys, C26 has the lowest chromium content (10 per cent) but possesses an unusually high aluminium content (11 per cent) which may account for its extremely good resistance to attack. In comparison, alloys 'C' and E474, possessing high chromium contents (17 and 27 per cent respectively) but no aluminium, show only fair corrosion resistance. Similarly the simple 60 per cent chromium 40 per cent nickel alloy had very poor resistance and was characterised by a loosely-adherent scale. However, EPD13 having similar composition to Nimonic 80A but with additional chromium (30 per cent total) generally had good corrosion resistance. The first batch (A) of EPD13 alloy supplied by the manufacturer (Henry Wiggin and Company Limited) was found to have inferior corrosion resistance to material subsequently supplied (Batch B). However analysis indicated that both batches were from the same melt.

Apparently a high chromium content alone is insufficient to ensure good resistance to sea-salt corrosion. Alloys with low chromium contents are very susceptible to attack (e.g., Nimonic 100 and Nimocast 258). It may be inferred that alloys low in chromium (e.g., Alloy C26) require higher aluminium contents than that present in Nimonic 100 to ensure equivalent corrosion resistance to those containing moderate or high chromium contents (e.g., 15 to 20 per cent in Nimonics 75, 80A, 90, 105 and 115).

Nimonic 75 contains negligible aluminium or titanium but the absence of molybdenum and tungsten which are found in substantial amounts in several of the alloys tested may account for its good corrosion resistance. The presence of 6 per cent molybdenum and 7 per cent tungsten respectively in the cobalt-base alloys 422/19 and X40 may account for their poor resistance to corrosion attack. In comparison, another cobalt alloy Umco 50, which contains no molybdenum or tungsten, showed good resistance. Under normal oxidising conditions, however, moderate additions of tungsten and molybdenum are not generally considered to have an adverse effect on the oxidation resistance of either nickel or cobalt alloys. However, their ability at elevated temperatures (above 800°C) to promote catastrophic oxidation is well known.

Two theories have been proposed to account for this effect with alloys containing at least 4 per cent of molybdenum. One theory[18] proposes the formation of low melting point oxide eutectics. Molybdenum trioxide melts at 790°C and the molybdenum trioxide/iron oxide eutectic, for example, melts at about 730°C. The presence of a liquid phase on the surface of an alloy has a most deleterious effect on oxidation resistance. Severe oxidation in still air above 800°C has also been attributed[19] to the possible dissociation of molybdenum trioxide into molybdenum dioxide and very reactive nascent oxygen ($MoO_3 \rightleftharpoons MoO_2 + {}^\prime O^\prime$). The large amount of oxygen available in moving air effectively prevents the formation of the lower molybdenum oxide. Any inability or difficulty to form a truly protective scale in simulated sea-salt conditions might well be accentuated by the formation of, for instance, molybdenum trioxide.

A series of tests was carried out at a higher testing temperature viz. 1000°C using similar salt and sulphur dioxide contents (i.e., 5 p.p.m. and 0.045 per cent respectively). A slight increase in the corrosion rate was apparent (see Table IV) but no alteration in the order of merit resulted for the limited number of alloys available for comparison.

Perhaps of more significance were the results of tests carried out at 950°C with a considerably increased sodium chloride and sulphur dioxide contents viz. 50 p.p.m. and 0.45 per cent respectively. These concentrations are about x100 greater than those likely to be encountered by aircraft gas turbines operating over the sea. Inspection of the results given in Table V, where comparison can also be made with similar laboratory tests at lower vapour concentrations, immediately reveals a very severe increase in corrosion for most alloys. Under such extreme conditions even the most resistant alloy, EPD13, experienced significant attack (weight loss of 6.9 mg/cm^2). Even more noteworthy is the poor resistance to corrosion exhibited by alloys such as Nimonic 105, Nimonic 115 and C26 which had shown up very favourably in the earlier tests with lower salt and sulphur dioxide concentrations.

The results of half-immersion tests using a salt mixture of 75 per cent sodium sulphate, and 25 per cent sodium chloride are given in Table VI.   Alloys tested for 1 hr at 950°C were either unattacked or severely corroded.   The results bear little relationship to those obtained in the simulated laboratory tests at the same temperatures, as seen by the markedly different orders of merit (see Table VI).

Considering the long durations of testing (up to 100 hr or more), results obtained at 950°C with 5 p.p.m. concentration show reasonable reproducibility for specimens experiencing relatively small amounts of corrosion (i.e., less than about 5 mg/cm² weight loss after descaling). However alloys experiencing quite severe attack i.e., E474 and chromium/ nickel (60/40) showed fairly large scatter in the few tests carried out. Generally only a few samples of each alloy were tested and accurate assessment of the reproducibility of this type of test can only be achieved by testing, say, 10 samples of each alloy at a given test tem- perature and vapour concentration.

6.0   Discussion of mechanism of attack

Both laboratory and engine tests have shown that the presence of sodium sulphate in the gas turbine resulting from sea-salt ingestion can lead to a characteristic attack known as 'sea-salt' corrosion.   It has been demonstrated at N.G.T.E., and by other investigators, that sodium sulphate alone is quite unreactive when in contact with nickel alloy specimens, but, the presence of a suitable triggering agent can result in severe corrosion of alloy specimens.   A mechanism has been proposed by Simons et al[20] for the corrosion of alloy steels in the presence of sodium sulphate.   It is thought that a similar mechanism of attack may apply in the corrosion of rotor and stator blades of gas turbines operating over the sea and is developed below.

Interaction between sodium chloride (from the sea-salt) and sulphur (from the fuel) occurs in the combustion chamber of the gas turbine, and can be written in the following simplified form.

$$2NaCl + 'S' + 2'H' + 2O_2$$

$$\rightarrow Na_2 SO_4 + 2HCl \qquad\qquad \dots\dots (1)$$
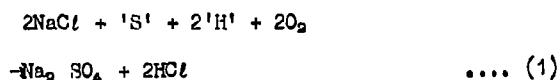
The sulphur and hydrogen are available from the combusting fuel either in the nascent form as in Equation (1) or in combination with oxygen as sul- phur dioxide and water vapour.   Free energy (ΔG) considerations predict that this reaction is thermodynamically possible but, of course, do not give any real indication of the reaction kinetics.

The combustion products containing sodium sulphate vapour, hydro- chloric acid vapour, water vapour, sulphur dioxide, sulphur trioxide, and incandescent carbon particles pass from the combustion chamber into the first stages of the turbine where some of the sodium sulphate and carbon are deposited on the relatively cool blade surfaces.   The initial triggering action involves reduction of the sodium sulphate by a reduc- ing agent, such as carbon, present in the deposit and may be represented as follows:-

$$2Na_2SO_4 + 6C + 3O_2 \rightarrow 2Na_2O + 6CO_2 + 2'S' \qquad \dots (2)$$
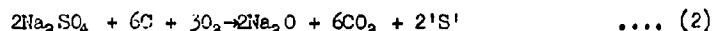
At a blade temperature of about $1000^{\circ}C$ thermodynamic considerations show that this reaction should readily occur. The free energy change (ΔG) is about -80 Kcal/mole.

The sulphur product formed in Equation (2) is immediately free to combine with the underlying blade alloy to form metal sulphides, thus:-

$$2 Cr + 3 'S' \rightarrow Cr_2S_3 \qquad \dots (3)$$

and possibly $\quad Ni + 'S' \rightarrow Ni S$
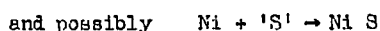
Chromium sulphide forms more readily than nickel sulphide because of the considerably greater reactivity of chromium (and therefore greater free energy of reaction). However, if the chromium content of the alloy is low the abundance of nickel available for reaction enables nickel sulphide to form (Law of Mass Action). A similar situation may also arise where chromium may be depleted at the surface layer by oxidation or at grain boundaries by carbide precipitation, or during severe corrosion where locally the chromium content may be reduced to a low level due to excessive chromium sulphide formation. However, loss of chromium from the alloy matrix through sulphide formation produces a concentration gradient between the corroded zone and the bulk of the alloy. Because of this, chromium diffusion into the areas denuded of chromium occurs and becomes available for further sulphide formation. Any nickel sulphide so formed is therefore likely to be reduced by newly available chromium:-

$$3 NiS + 2 Cr \rightarrow Cr_2S_3 + 3 Ni \qquad \dots (4)$$
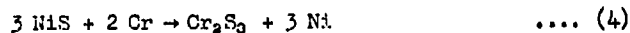
This explanation of sulphide attack is borne out in service where nickel sulphide is not usually found in the corrosion products.

The metal sulphide formed in the above way is now available to combine with either free sodium sulphate or free oxygen in the combustion products of the gas turbine. The reaction between chromium sulphide and sodium sulphate,

$$Na_2SO_4 + Cr_2S_3 \rightarrow Cr_2O_3 + Na_2O + 4S \qquad \dots (5)$$
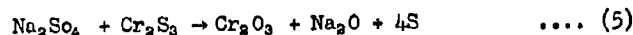
has been proposed by other investigators[22]. However, free energy considerations give no support to this theory since the reaction would involve a large and positive energy change ($+\Delta G$). More correctly, Equation (5) should be written with reactants and products reversed. A similar situation occurs with nickel substituted for chromium.

It is more likely that the relatively simple reaction between chromium sulphide and oxygen

$$2Cr_2S_3 + 9O_2 \rightarrow 2Cr_2O_3 + 6SO_2 \qquad \qquad \dots\dots (6)$$

will occur.

This reaction is strongly possible from thermodynamic consideration and has also been reported in the literature[21]. The formation of chromium sulphate is also possible. However, a limited supply of oxygen may be essential for sulphate formation,

$$Cr_2S_3 + 6O_2 \rightarrow Cr_2(SO_4)_3$$
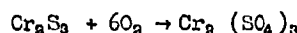
Nickel oxide, with chromic oxide in the outer loosely-adherent scale may be readily formed by combination of nickel from the blade alloy (which has been heavily impoverished of protective chromium) with oxygen in the following way:-

$$2Ni + O_2 \rightarrow 2NiO$$
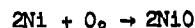
This proposed mechanism, based on thermodynamic considerations has not included the many side reactions which are quite likely to occur. It does, however, give a reasonable outline of the corrosion attack involving formation of a reactive sulphur species through reduction of sodium sulphate deposits on the blade surface. It is this sulphur species which readily combines with the underlying blade alloy to form sulphide fingers that penetrate into the matrix and eventually become available for enhanced oxidation.

The formation of nickel/nickel sulphide eutectic with a particularly low melting point (644°C) has been proposed by investigators as being the cause of enhanced oxidation[15,20]. The theory suggests that metal dissolved in the eutectic mixture would be highly reactive towards oxygen especially as a truly protective film seldom forms on a liquid. The two stage oxidation process may be written as follows:-

(i)   Solution of metal $Ni + NiS \rightarrow Ni/NiS$ eutectic

(ii) Oxidation $Ni/NiS + \tfrac{1}{2}O_2 \rightarrow NiO + NiS$

This mechanism postulates oxidation of the nickel dissolved in the eutectic rather than the nickel sulphide.

Generally, no evidence is found that a liquid phase has formed during corrosion in service at say, 850°C. This is not unreasonable if chromium sulphide is formed preferentially to nickel sulphide. Chromium sulphide (melting point 1550°C) does form a metal/metal sulphide eutectic which melts at 1350°C, a temperature considerably higher than that encountered by rotor or stator blades in service. The formation of a low melting nickel/nickel sulphide phase (644°C) is often identified in laboratory half-immersion tests using sodium sulphate/sodium chloride mixtures[14,15], and especially when attack is severe.

Experimental data indicates that the aluminium content of typical nickel-base alloys appears to have a significant influence on resistance to sea-salt corrosion, especially with alloys low in chromium. The oxidation resistance of typical nickel-base alloys (i.e., the Nimonic series) is known to be accounted for by the physical characteristics of the chromic oxide/nickel oxide layer formed on the alloy surface. With chromium contents of 10 per cent or more a 'spinel' type structure is formed between the nickel oxide and chromic oxide which is extremely impervious to oxygen and is tenaciously held to the alloy surface. Additions of aluminium to nickel-chromium alloys result in a further spinel being formed between the nickel oxide and aluminium oxide which is considered to give even greater protection to the underlying alloy. A non-spinel type structure is also formed between the chromic oxide and aluminium oxide which is less protective.

Alloys of low or zero aluminium content depend entirely on the nickel oxide/chromic oxide spinel for protection of the substrate against oxidation. Damage to this protective spinel does not result in rapid oxidation of the alloy because fresh imporvious spinel is immediately formed through oxidation of the alloy surface. However, the absence of chromium in the surface layers of the alloy through sulphide formation results in the nickel matrix being exposed to severe oxidation, because nickel oxide alone affords no protection above $800^{\circ}C$.

Laboratory tests have indicated that adequate percentages of aluminium have a beneficial effect on the resistance of nickel alloys to sea-salt corrosion. It is suggested that aluminium may do this by being unable to form a stable sulphide under the prevailing conditions. Aluminium would, therefore, always be available in the surface layers of the alloy to form aluminium oxide which alone, or in combination with nickel oxide as a spinel, would act as a protective barrier against the corrosive environment. Evidence as to the ability of aluminium to form a stable sulphide is rather scanty and there is certainly no useful thermodynamic data available. Several investigators[22] have reported that aluminium sulphide readily decomposes in air and is reduced by iron and copper. It appears therefore that aluminium sulphide is unlikely to be found in corrosion products but may break down to form protective aluminium oxide. Several investigators have experimented with aluminised and chromised coatings on typical gas turbine rotor blade alloys (e.g., Nimonic 90 and Nimonic 115) in both full scale rig[23] and laboratory half-immersion tests[14,24]. Pack cementation techniques are preferred for applying the coating. In half-immersion tests using the most reactive salt mixture (75 per cent sodium sulphate, 25 per cent sodium chloride) coatings generally had lives of from 1 to 16 hr at $900^{\circ}C$. In rig tests, aluminised coatings remained protective for up to 20 hr. A single laboratory test at N.G.T.E. using a pack aluminised Nimonic 90 specimen under simulated conditions with a salt concentration of 25 p.p.m. (sulphur dioxide 0.225 per cent) indicated that the coating gave satisfactory protection at $950^{\circ}C$ for the test duration (100 hr).

7.0   Further work

Investigatory work at N.G.T.E. into the resistance of high temperature alloys to sea-salt corrosion was prompted by the need to substantiate the claim of the United States Navy that cobalt alloys had superior resistance to nickel alloys. Research has gone further than this and attempts have been made to shed further light on the mechanism of attack and the

factors influencing the corrosion resistance of the various alloys tested.
Three lines of further research are possible.

(a)   More accurate determination of the influence of alloy com-
        position on corrosion resistance using alloys with con-
        trolled additions.

(b)   More comprehensive research into the influence of atmosphere
        composition and concentration in promoting corrosion at
        elevated temperatures in simulated laboratory tests.

(c)   The development and evaluation of coatings that are resist-
        ant to sea-salt corrosion.

8.0   Conclusion

        A laboratory test in which air, sodium chloride vapour, etc., are
passed over various high temperature alloys has been shown to reproduce
corrosion in the laboratory similar to that which occurs in gas turbines
operating over the sea.   The results obtained do not substantiate the
original United States Navy contention that cobalt-base alloys have
superior corrosion resistance to nickel-base alloys.   The susceptibility
of nickel alloys to corrosion under simulated laboratory conditions
generally appears to be influenced by the aluminium and chromium contents
of the alloys and is in agreement with the corrosion mechanism proposed.

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25	L. W. Johnson E. J. Bradbury	Corrosion resistant materials in marine engineering. The International Nickel Company (Mond) Limited Publication No. 5880/5911
26	F. E. Fowle	Smithsonian Physical Tables. Vol. 88 page 651, Published by Smithsonian Institution 1934

TABLE I

Chemical analysis of scale on Ashanti turbine blades

Element	Per cent by weight of elements in scale				Typical Composition of Nimonic 90 and Nimocast 90
	First-stage stator blades (Nimocast 90)		First-stage rotor blades (Nimonic 90)		
	No. 2	No. 4	A	B	
C.C.I. Woolwich spectrographic analyses					
Al	10.0	8.0	11.5	9.5	1.2
B	1.0	1.0	<0.5	<0.5	-
Cd	SLIGHT		TRACE		
Co	6.0	4.5	3.5	3.0	16.0
Cr	20.0	15.5	9.0	7.5	20.0
Cu	1.5	1.0	1.5	1.5	0.5
Fe	10.0	8.0	23.0	19.5	5.0
Mn	<0.5	<0.5	<0.5	<0.5	0.3
Ni	25.0	24.0	17.5	14.5	BAL
Pb	1.5	1.0	2.5	2.0	-
Ti	<1.0	<1.0	2.5	2.0	2.4
V	0.5	0.5	0.5	0.5	-
Si	-	-	4.0	3.0	0.4
N.G.T.E. Analyses					
Si	$(0.7)^*$		-	-	
SO_3	12.5	9.0	24.1	24.3	
Na	0.7	0.5	3.1	3.4	

N.B. *From analysis of a portion of scale taken from another first-stage stator blade (No. 6)

TABLE II

Chemical analyses of samples of sea water
at two localities

| Constituent | Concentration in parts per million | |
| | Locality of sampling | |
	Kure Beach[25] North Carolina	North Pacific[26]
Sodium	10,590	10,722
Chlorine	19,200	19,337
Magnesium	1,292	1,207
Calcium	404	417
Potassium	403	382
Sulphate, SO_4	2,664	2,705
Bromine	67	66
Iron	negligible	-
Carbonate, CO_3	negligible	7
pH	7.7	-

TABLE III

Results of simulated laboratory sea-salt corrosion tests at 950°C with 5 p.p.m. salt concentration

Gas flow rates and conditions:-

Air saturated with water vapour	4 litres/min
Sulphur dioxide	0.045 per cent by volume
Sodium chloride	5 p.p.m. by weight

A graphite coating was applied to all specimens prior to testing.

Alloy	Test duration hours	Weight loss* mg/cm²
Ni-base		
Nimonic 75	72	3.7
	100	2.5
Nimonic 80A	72	6.9
	100	3.3
	100	6.0
	250	8.1
Nimonic 90	72	4.6
	100	3.8
	100	4.4
Nimonic 100	72	36.3
Nimonic 105	100	1.6
	100	1.7
	150	1.3
Nimonic 115	100	1.6
	100	4.3
Nickel/Chromium (80/20)	100	1.1
	100	2.9
Nimocast 258	72	101.0
EPD13 (Batch A)	72	8.7
	72	15.8
EPD13 (Batch B)	100	3.7
	116	0.9
	116	3.6
E474	100	4.9
	100	29.1

TABLE III (cont'd)

Alloy[✗]	Test duration hours	Weight loss[*] mg/cm²
Alloy C	76	8.5
Chromium/Nickel (60/40)	76	20.8
	100	8.5
	100	22.7
	100	51.0
Alloy C26	76	0.0
	100	0.3
Co-base		
Umco 50 (cast)	100	0.0
Umco 50 (forged)	100	2.3
	100	3.5
X40 (cast)	24	4.5
	72	16.3
	100	17.4
422/19	24	3.3
	100	17.6

[✗] See Appendix I for compositions used

[*] See Appendix II for methods for scale removal after testing

TABLE IV

Results of simulated laboratory sea-salt
corrosion tests at 1000°C with
5 p.p.m. salt concentration

Gas flow rates and conditions:-

Air saturated with water vapour	4 litres/min
Sulphur dioxide	0.045 per cent by volume
Sodium chloride	5 p.p.m. by weight

A graphite coating was applied to all specimens prior to testing.

Alloy	Test duration hours	Weight loss mg/cm^2
Nickel-base		
Nimonic 75	100	4.2
Nimonic 115	100	2.6
EPD13 (Batch B)	24	2.7
	100	5.5
Cobalt-base		
Umco 50 (forged)	24	6.0
	100	9.0
X40	100	40.4

TABLE V

Comparative performance of various nickel and cobalt alloys in simulated laboratory corrosion tests at 950 and 1000°C

Gas flow rates and conditions:-

Air saturated with water vapour	4 litres/min
Sulphur dioxide	0.45 per cent by volume
Sodium chloride	50 p.p.m. by weight
Test duration	100 hours

A graphite coating was applied to all specimens prior to testing.

Alloy	Weight loss mg/cm²		
	50 p.p.m. salt concentration 950°C	5 p.p.m. salt* concentration 950°C	5 p.p.m. salt† concentration 1000°C
Ni-base			
Nimonic 75	12.2	2.5	4.2
Nimonic 90	59.4	3.8;4.4	-
Nimonic 105	91.4	1.6;1.7	-
Nimonic 115	106.0;211.7	1.6;4.3	2.6
EPD13 (Batch B)	6.9	3.7;~0.9;~3.6	5.5
E474	42.3	4.9;29.1	-
Alloy C	111.1	>8.5	-
Chromium/Nickel (60/40)	44.3	8.5;22.7;51.0	-
Alloy C26	95.3	0.3	
Co-base			
Umco 50 (cast)	26.0	0.0;2.5	-
Umco 50 (forged)	3.0	3.5	9.0
422/19	5.0	17.6	-
Cobalt/Chromium (80/20)	24.0	-	-

*Results from Table III
†Results from Table IV

TABLE VI

Results of laboratory half-immersion corrosion
tests in sulphate/chloride mixtures

Test conditions   Composition of salt mixture

                            sodium sulphate 75 per cent

                            sodium chloride 25 per cent

Test temperature $950^{\circ}C$

Duration   1 hour

Alloy	Weight loss mg/cm^2	
	Half-immersion test	Simulated laboratory* test 100 hr/950°C
Ni-base		
Nimonic 90	211	3.8;4.4
Nickel/Chromium (80/20)	0.4	1.1;2.9
E474	0.7	4.9;29.1
Alloy C	12.8	>8.5
Chromium/Nickel (60/40)	0.6	8.5;22.7;51.0
Alloy C26	126	0.3
Co-base		
Umco 50 (cast)	145;155	0.0;2.3
Umco 50 (forged)	2.2;3.1	3.5
X40	<1.0	17.4
422/19	<1.0	17.6

*Results from Table III

APPENDIX I

Typical compositions of various alloys tested

Alloy	Heat treatment and/or condition	Percentage								
		C	Cr	Co	Ti	Al	Ni	Fe	Mo	W
Nimonic 75		0.11	18/21	—	0.7	0.5/1.8	BAL	1.75	—	—
Nimonic 8CA		0.1	18/21	2	1.8/2.7	1.43	BAL	—	—	—
Nimonic 90	(a)	0.05	18/21	15.9	2.6	4/6	BAL	0.86	—	—
Nimonic 100		0.2	10/12	20	1/2	—	BAL	—	—	—
Nimonic 105		0.13	13.5/16	19.9	1.6	4.39	BAL	0.56	4.6	—
Nimonic 115		0.15	15	15.1	4.1	4.95	BAL	—	3.25	—
Nickel/Chromium (80/20)	As cast	0.2	20	—	—	—	BAL	—	—	—
Nimocast 258	As cast	0.2	10	20	3.7	4.8	BAL	—	—	—
EPD13 (Batch A)	As rolled	0.05	29.1	<0.2	1.79	0.71	BAL	0.24	—	—
EPD13 (Batch B)										
E47	As cast	2.0	27	16	—	—	54	4.0	—	17
Alloy C	As cast	0.1	17	—	—	—	BAL	—	6.0	5.0
Chromium/Nickel (60/40)	As cast		60				40			
Alloy C26	As cast	0.1	10	—	—	11	BAL	—	2.0	—
Umco 50 (cast)	As cast	0.5	30	BAL	—	—	—	20	—	—
Umco 50 (forged)	As rolled	0.06	30	BAL	—	—	—	20	—	—
X40	As cast	0.46	25	BAL	—	—	10	—	—	7.3
422/19	As cast	0.39	25	BAL	—	—	16	—	6.1	—

(a) Alloys in fully heat treated condition as specified in:-

(i) The Nimonic Series of High Temperature Alloys by Henry Wiggin and Company Limited Publication No. 2358, August 1961.

(ii) The Nimonic Alloys, Design Data. Henry Wiggin and Company Limited Publication No. 1303, September 1957.

APPENDIX II

Methods applied for descaling of nickel and
cobalt alloys after corrosion testing

(a)   Electrolytic descaling in molten sodium hydroxide, sodium carbonate
        mixture (50/50) at 450°C. The corroded specimen was made the
        cathode, and its nickel container used as the anode. Reduction
        of the metal oxides to the metal by sodium ions occurred, the
        reduced metal being removed by brushing. Metal sulphides were
        similarly reduced.

$$NaOH \rightleftharpoons Na^+ + (OH)^-$$

At cathode $$NiO + 2Na^+ \rightarrow Ni + Na_2O$$

$$Na_2O + H_2O \rightarrow 2NaOH$$
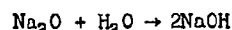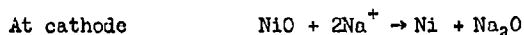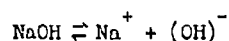
        However this method was not found entirely satisfactory for cobalt
        alloys as they were susceptible to greater uncorroded metal loss.
        Other techniques were therefore used for these alloys.

(b)   Immersion in a warm (60/70°C) acidified sodium fluoride solution,
        made by dissolving 4 grams of sodium fluoride in a mixture of
        10 mls conc. HNO_3 and 86 mls water.

        This technique was very effective for cobalt Umco 50 alloy but
        additional abrasion was necessary with other cobalt alloys.

(c)   Electrolytic descaling in diluted 5 per cent sulphuric acid
        solution was found to be quite effective for scale removal with
        most specimens corroded in sulphate-chloride salt mixtures. The
        specimen is made the cathode and the presence of an inhibitor,
        diortho-thiotolylurea, further minimised uncorroded metal loss
        through acid attack. Scale removal results from the prising
        effect of hydrogen evolved at the metal/scale interface.

REP 10-65

FIG. 1
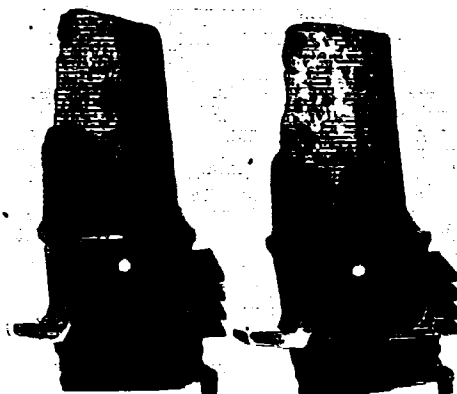
CORRODED NIMONIC 100 ROTOR BLADE
REMOVED FROM GAZELLE 101 ENGINE
AFTER SALT WATER INGESTION TRIALS.

FIG. 2

LOOSELY ADHERENT
SCALE.

INTERMEDIATE PARTLY
OXIDISED LAYER.

FINELY DISPERSED
'AHEAD' LAYER
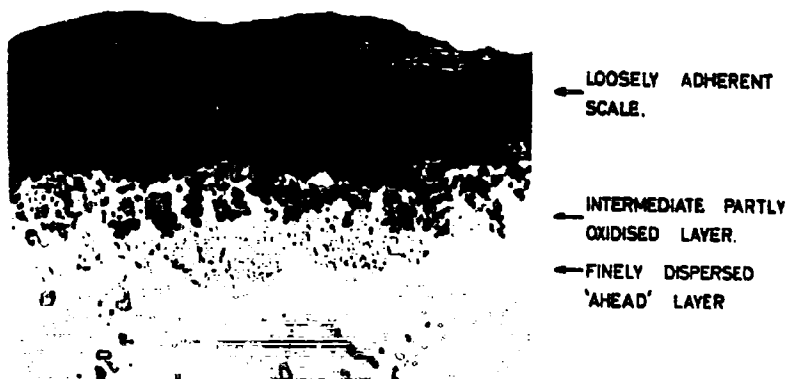
SECTION THROUGH CORRODED AREA
ON NIMONIC 100 BLADE.

FIG. 3

VIEW OF NIMONIC 90 ROTOR BLADE
REMOVED FROM BRISTOL PROTEUS ENGINE
AFTER OVER 700 HRS OPERATION
IN H.M.S. BRAVE BORDERER.

FIG. 4

SECTION THROUGH SURFACE PITTING
ON NIMONIC 90 BLADE CLEARLY REVEALING
SULPHIDE PENETRATION INTO THE ALLOY.

FIG. 5

REP 12-65

FIRST   STAGE   NIMONIC   90   STATOR   SEGMENT

REMOVED   FROM   MARINE   PROTEUS   ENGINE

AFTER   SEVERE   SEA - WATER   INGESTION
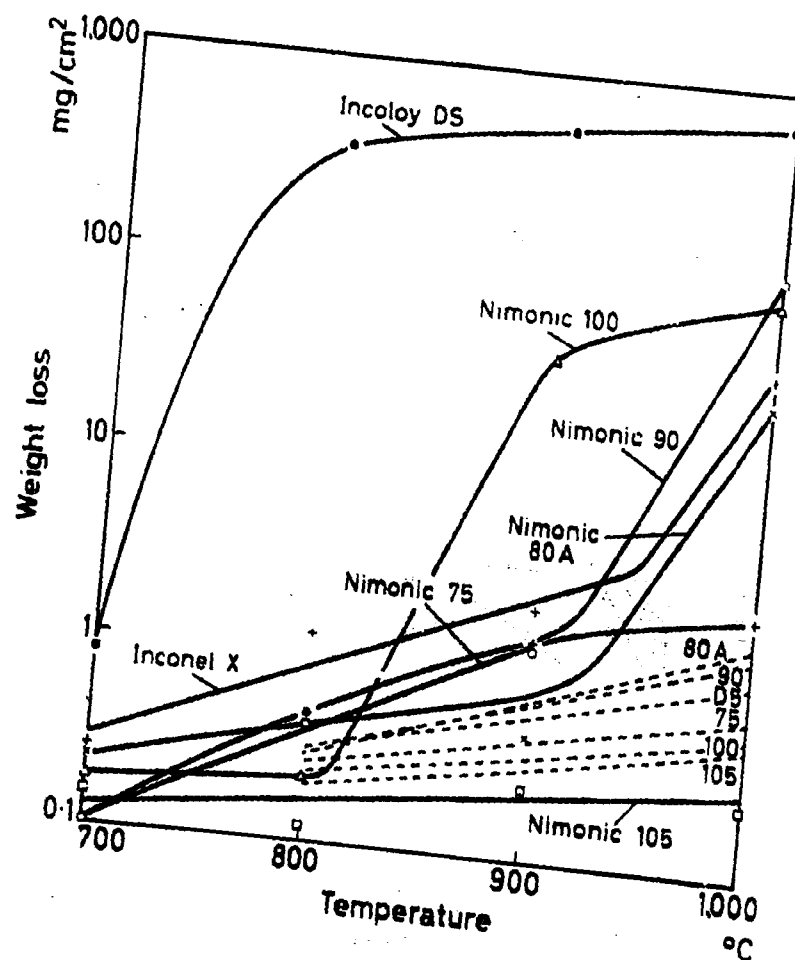
FIG. 6

REP 13-65

(BROKEN LINES SHOW OXIDATION IN AIR.)

EFFECT OF TEMPERATURE ON THE CORROSION RESISTANCE OF VARIOUS NICKEL BASE ALLOYS TO SODIUM SULPHATE, 0.5 PER CENT SODIUM CHLORIDE MIXTURES

FIG. 7
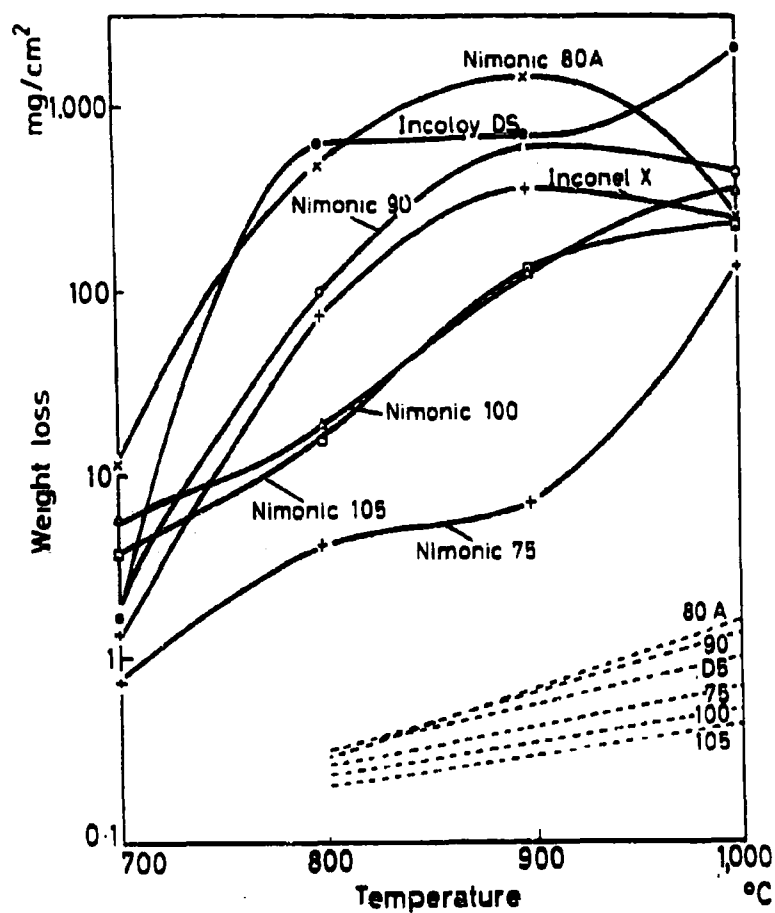
(BROKEN LINES SHOW OXIDATION IN AIR.)

EFFECT OF TEMPERATURE ON THE CORROSION RESISTANCE OF VARIOUS NICKEL BASE ALLOYS TO SODIUM SULPHATE, 25 PER CENT SODIUM CHLORIDE MIXTURES

SK 85074

FIG. 8

ALUMINA TUBE 1½ INCHES
OUTSIDE DIAMETER

EXHAUST

TUBE B

ALLOY SPECIMEN
HEATED TO 950 °C

18 INCHES

SULPHUR DIOXIDE
SUPPLY

18 INCHES

TUBE A

SODIUM CHLORIDE LUMPS AT 615 °C
TO GIVE 5 ppm CONCENTRATION IN GAS STREAM

AIR SATURATED WITH
WATER VAPOUR

FURNACE ELEMENTS GIVING CLOSE
TEMPERATURE CONTROL (±7°C) OVER
MUCH OF LENGTH
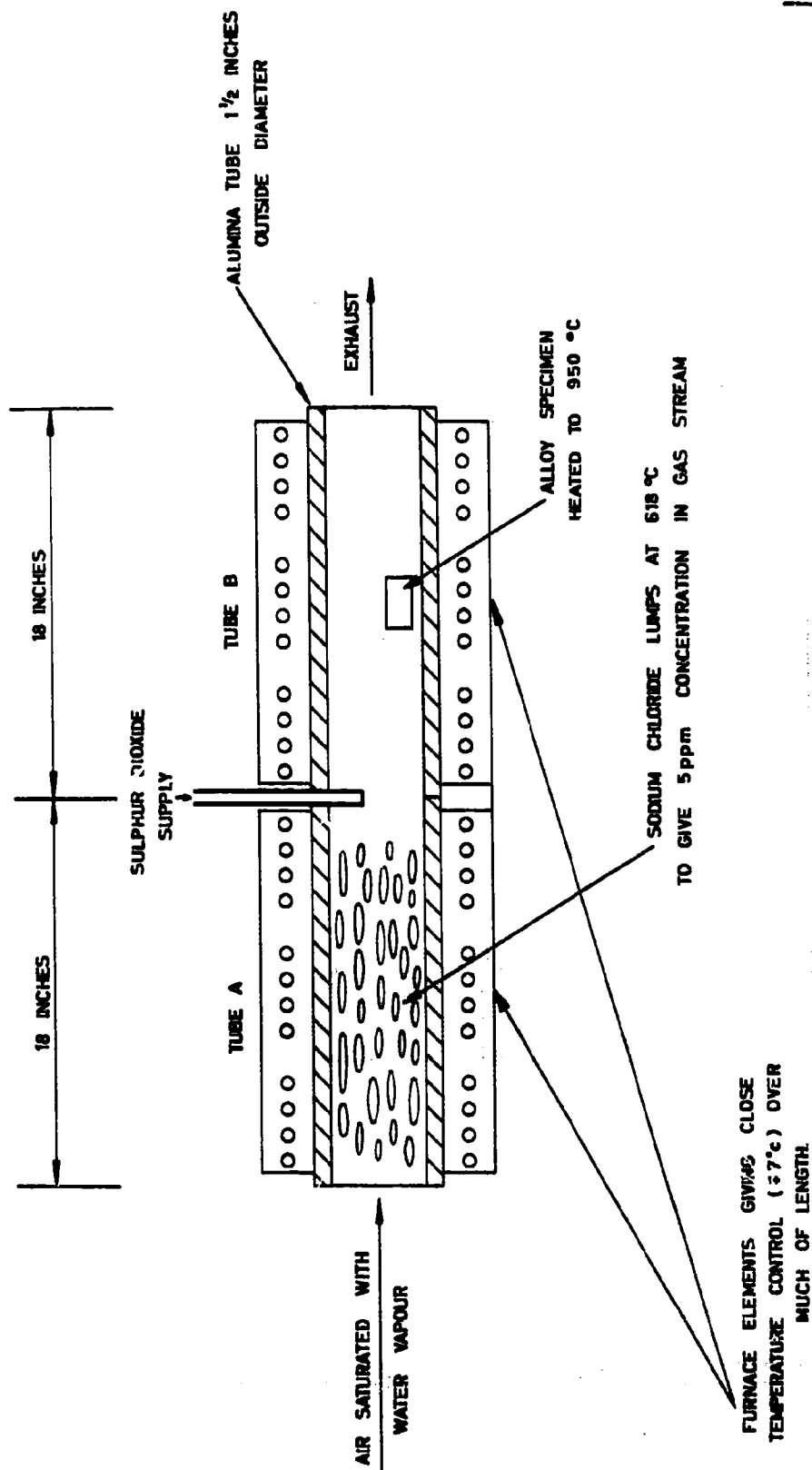
APPARATUS FOR PRODUCING SIMULATED

SEA–SALT CORROSION CONDITIONS IN THE LABORATORY

FIG. 9
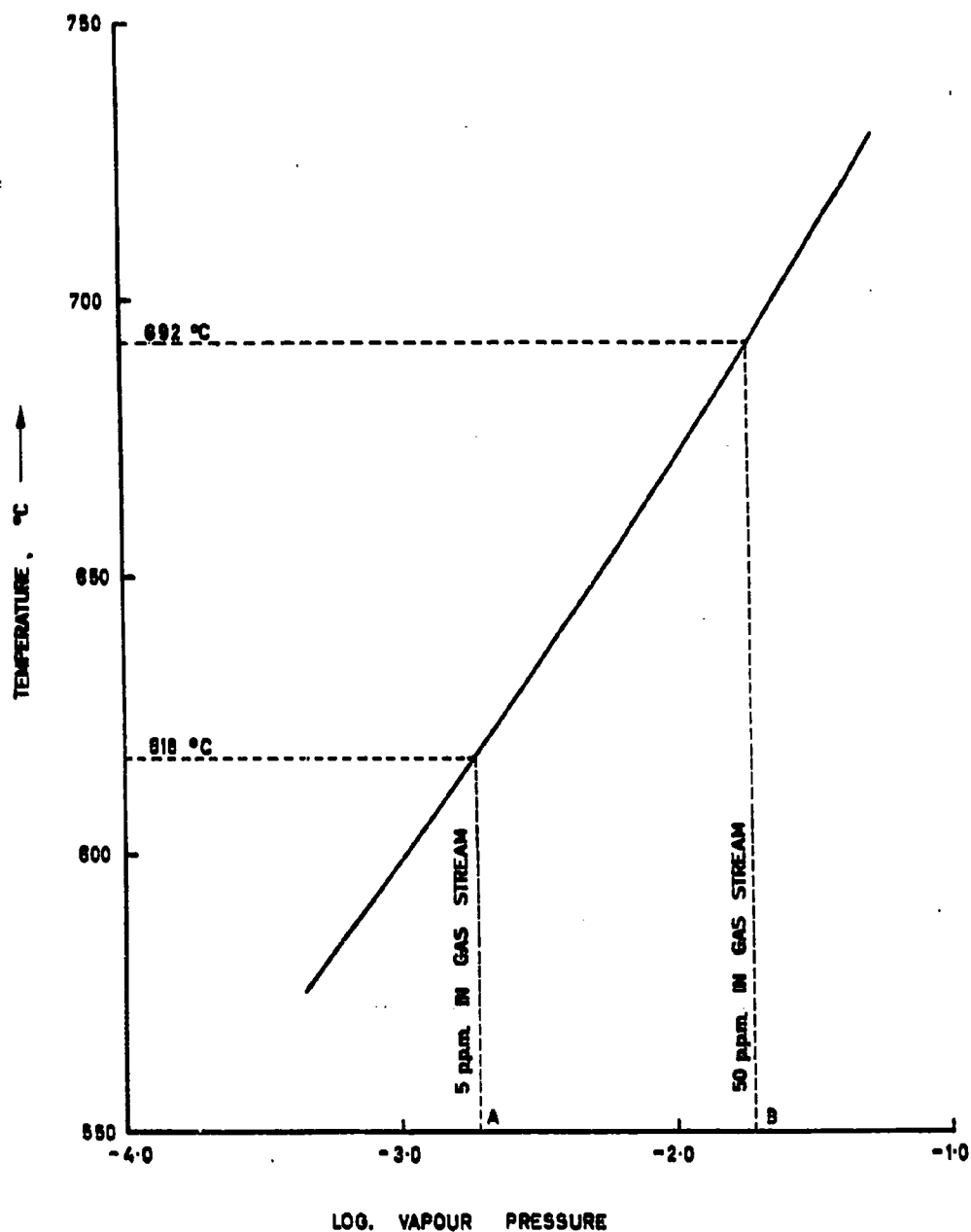
VARIATION OF VAPOUR PRESSURE

WITH TEMPERATURE FOR SODIUM CHLORIDE

FIG. 10

REP 15-65
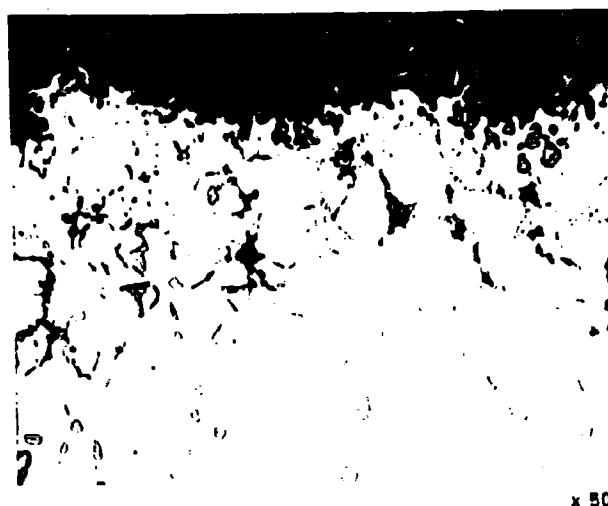
OUTER CORROSION
LAYER CONSISTING
OF OXIDE + SULPHID

x 500

NICKEL EPD 13 ALLOY (BATCH A)
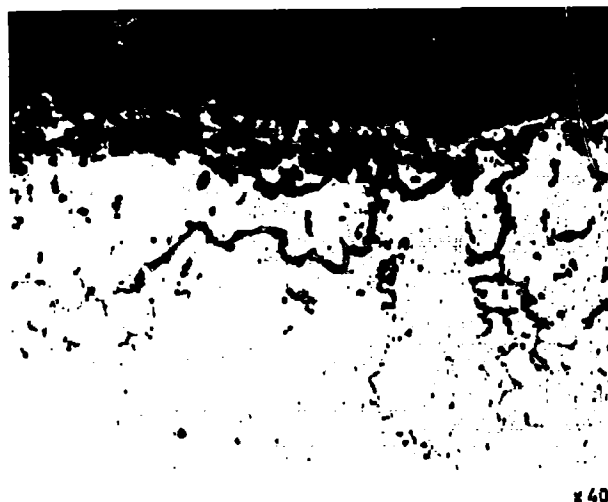
OUTER CORROSION
LAYER CONSISTING
OF OXIDE + SULPHIE

SEVERE PENETRATIO
INTO UNDERLYING
MATRIX

x 400

COBALT X40 ALLOY

SECTIONS THROUGH VARIOUS NICKEL & COBALT BASED
ALLOYS SHOWING NATURE OF CORROSION ATTACK
AFTER 100 HR TEST AT 950°C WITH A SALT
CONCENTRATION OF 5 PARTS PER MILLION.

FIG. 10 (cont.)

REP 16-65
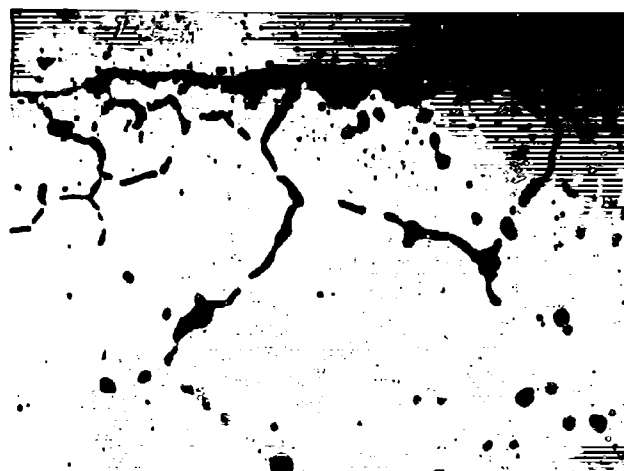
← METAL STRIP
SUPPORTING
SPECIMEN SURFACE

← SULPHIDE + OXIDE
PENETRATION INTO
ALLOY

x 900

COBALT UMCO 50 ALLOY (FORGED)

FIG. II

REP 17-65

OUTER OXIDE LAYER

INTERMEDIATE OXIDE + SULPHIDE LAYER

x 250

NIMONIC 115 ALLOY

SULPHIDE PARTICLES BENEATH SPECIMEN SURFACE

x 900
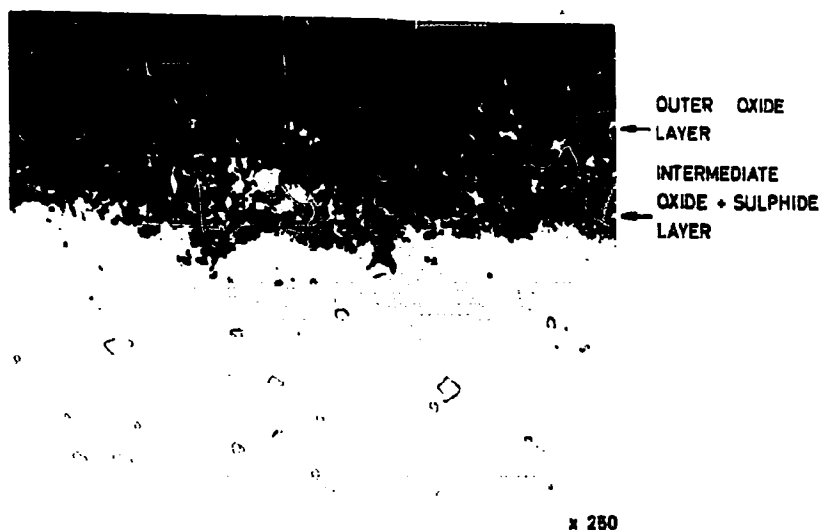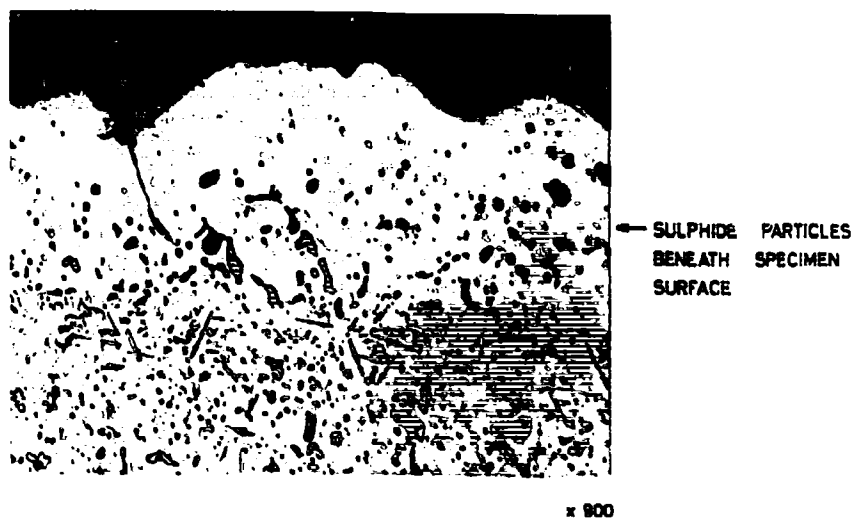
NICKEL C26 ALLOY

SECTIONS THROUGH ALLOY SPECIMENS

AFTER 100 HR CORROSION TEST AT 950 °C

WITH A SALT CONCENTRATION OF 50 PARTS PER MILLION

RESTRICTED

National Gas Turbine Est. Report No. R.257
1955.5
Dean, A. V.

620.19:669.255:
669.245

INVESTIGATION INTO THE RESISTANCE OF
VARIOUS NICKEL AND COBALT BASE ALLOYS
TO SEA-SALT CORROSION AT ELEVATED TEMPERATURES

Gas turbines operating in salt laden atmospheres (i.e., over the sea) occasionally encounter severe corrosion of the turbine blades. The cause of this attack is attributed to ingested sea-salt combining in the combustion chamber with the sulphur in the fuel to form sodium sulphate which is deposited on the turbine blades and leads to corrosive attack. Laboratory investigations at N.G.T.E. have involved the passage over heated specimens of the vapours and gases (e.g., sodium chloride and sulphur dioxide) that were thought most likely to cause corrosion. Tests at 950°C indicated that nickel-base alloys low in chromium were very susceptible to attack, but that a high chromium content alone was insufficient to ensure good corrosion resistance. However, the presence of adequate amounts of P.T.O.

RESTRICTED

RESTRICTED

National Gas Turbine Est. Report No. R.257
1955.5
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620.19:669.255:
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INVESTIGATION INTO THE RESISTANCE OF
VARIOUS NICKEL AND COBALT BASE ALLOYS
TO SEA-SALT CORROSION AT ELEVATED TEMPERATURES

Gas turbines operating in salt laden atmospheres (i.e., over the sea) occasionally encounter severe corrosion of the turbine blades. The cause of this attack is attributed to ingested sea-salt combining in the combustion chamber with the sulphur in the fuel to form sodium sulphate which is deposited on the turbine blades and leads to corrosive attack. Laboratory investigations at N.G.T.E. have involved the passage over heated specimens of the vapours and gases (e.g., sodium chloride and sulphur dioxide) that were thought most likely to cause corrosion. Tests at 950°C indicated that nickel-base alloys low in chromium were very susceptible to attack, but that a high chromium content alone was insufficient to ensure good corrosion resistance. However, the presence of adequate amounts of P.T.O.

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aluminium in the alloys appeared to be beneficial. The corrosion resistance of cobalt-base alloys was no better than that of nickel-base alloys.

A corrosion mechanism is proposed which involves the depletion of chromium from the surface of the alloy through sulphide formation so leading to a loosely-adherent nickel oxide film. Adequate percentages of aluminium in nickel-base alloys are thought to have a beneficial effect because aluminium does not form a stable sulphide and is therefore always available in the surface layers of the alloy to form protective aluminium oxide.